

# Long-range-interactions induced ordered structures in deposition processes

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We present a new model of sequential adsorption in which the adsorbing particles experience dipolar interactions. We show that in the presence of these long-range interactions, highly ordered structures in the adsorbed layer may be induced at low temperatures. The new phenomenology manifests through significant variations of the pair correlation function and the jamming limit, with respect to the case of noninteracting particles. Our study could be relevant in understanding the adsorption of magnetic colloidal particles in presence of a magnetic field.

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The study of the irreversible adsorption of colloidal particles onto a surface has been since long time subject of a great deal of interest, due to its potential applications to physical, physico-chemical, and biological problems [1]. Our global understanding of the process has been possible through the formulation of different models, analyzed either numerically or analytically. These models share a sequential and irreversible nature, and differ in the rules by which the particles accommodate when arriving at the surface. The various rules are responsible for the different values of the relevant quantities describing the adsorbed phase, such as the jamming limit, the pair correlation function, and the local variance of the number of deposited particles. In the random sequential adsorption (RSA) model [2–6] particles are placed at random positions on the substrate. If an incoming particle overlaps with a previously adsorbed one, it is rejected and a new one probed; otherwise it becomes irreversibly adsorbed. In the ballistic model (BM) [7–10] the particles descend to the surface following straight vertical trajectories. An incoming particle that does not reach the substrate is allowed to roll over the previously adsorbed, following the steepest descent path, until it reaches a stable position. Only particles that fail to gain the surface are finally rejected.

All these models, and their subsequent extensions, have been mainly implemented by considering short range—hard core—interactions among particles. With the exception of the analysis of the role played by electrostatic interactions [11], the case of long-range interactions remains essentially unexplored. Our purpose in this Letter is to analyze comprehensively the influence that these interactions have in the kinetics of deposition in a simple numerical model. We will show that when they are taken into account, a new aspect of the problem emerges. The structure of the adsorbed layer changes considerably, giving rise in some cases to the appearance of a higher degree of order in the substrate.

To illustrate this point, we will focus on the case of anisotropic dipolar interactions, and present numerical simulations of the adsorption process on a line ( $1+1d$ ) and on a plane ( $1+2d$ ). In our simulations we consider the adsorption of spherical magnetic particles of diameter  $a$  and magnetic moment  $\vec{\mu} = \mu\vec{u}$ , with  $\mu$  being the magnetic moment strength and  $\vec{u}$  a unit vector oriented along its direction. Orientation of dipoles is restricted to the space in which they diffuse:  $\mathbb{R}^2$  in ( $1+1d$ ) and  $\mathbb{R}^3$  in ( $1+2d$ ). The dipolar interaction between two particles  $i$  and  $j$ , located at positions  $\vec{r}_i$  and  $\vec{r}_j$ , respectively, is  $U_{ij} = \mu^2 E_{ij}/a^3$ , with  $E_{ij}$  being the dimensionless energy

$$E_{ij} = a^3 \left\{ \vec{u}_i \cdot \vec{u}_j - 3(\vec{u}_i \cdot \vec{r}_{ij})(\vec{u}_j \cdot \vec{r}_{ij})/r_{ij}^2 \right\} / r_{ij}^3, \quad (1)$$

where  $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ . Particles are released at random positions over a certain initial height  $z_{in}$ , having assigned an initial orientation  $\vec{u}_i^0$ . Each particle undergoes a random walk until it either becomes adsorbed or moves away from the substrate a distance greater than  $z_{out}$ ; in this case, the particle is removed and a new one released. The effect of the interactions is taken into account by means of a Metropolis algorithm [12–14]. Suppose there are  $N-1$  adsorbed particles, located at points  $\vec{r}_i$ ,  $i = 1, \dots, N-1$ . At some time  $t$  an incoming dipole occupies the position  $\vec{r}_N$  and has a total energy  $E = \sum_{i=1}^{N-1} E_{Ni}$ . At time  $t+1$  we compute a new position  $\vec{r}_N^*$ ; the particle arrives there by means of jump of length  $\delta$  in a direction chosen at random. The movement to  $\vec{r}_N^*$  is performed rigidly, without changing  $\vec{u}_N$ . The energy experienced in the new position is  $E^*$ , and the total change in the energy due to the movement is  $\Delta E = E^* - E$ . If  $\Delta E \leq 0$ , the movement is accepted; otherwise, it is accepted with probability  $p = \exp(-\Delta E/T_r)$ , where  $T_r = a^3 k_B T / \mu^2$  is a reduced temperature. Note that with this procedure we do not take into account gravitational forces. In order to speed up the algorithm, when an incoming particle reaches a position very close to the substrate (less than one diameter) it is attached according to the BM rules.

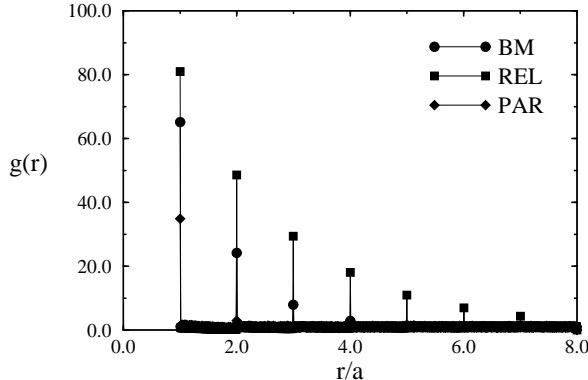


FIG. 1. Pair correlation function for dipolar adsorption, in the free limit  $T_r \rightarrow \infty$ , and for models REL and PAR at  $T_r = 0$ .

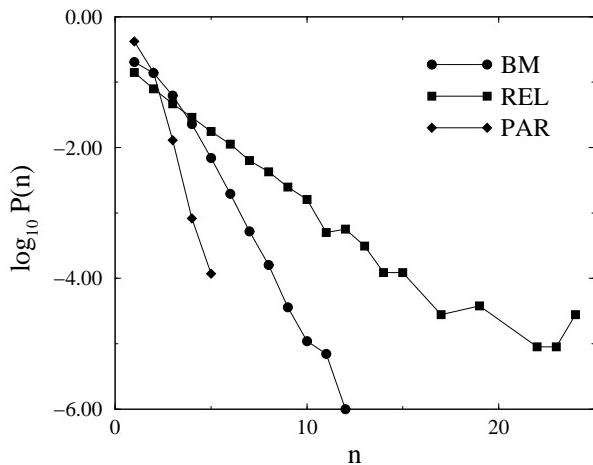


FIG. 2. Chain-length density function for dipolar adsorption, in the free limit  $T_r \rightarrow \infty$ , and for models REL and PAR at  $T_r = 0$ .

This procedure indeed assumes the presence of a strong short-ranged attraction between the substrate and the particles, which overcomes dipolar interactions at short distances.

The description of the algorithm is completed by prescribing the dynamics of the dipoles. We have considered two possibilities under scrutiny, defining two different models: (i) Relaxed dipoles (model REL). The initial orientation  $\vec{v}_i^0$  of the dipoles is assigned at random. After every accepted movement, the moment of the random walker is oriented along the direction of the total magnetic field on its position. After adsorption, a newly attached dipole undergoes a last relaxation, and its direction does not change any more. There are two natural choices for the orientation of the first adsorbed dipole: either select it randomly or parallel to the substrate. Both cases provide comparable results, within the error bars. The results reported here correspond to a random initial dipole. (ii) Parallel dipoles (model PAR). All dipoles are parallel to the substrate, pointing rigidly towards a pre-

determined fixed direction. Both models are actually the limits of a process of adsorption of relaxing dipoles in the presence of a magnetic field. Model REL is recovered in the limit of zero field, whereas model PAR corresponds to a very strong field.

In  $(1+1d)$  we have simulated the adsorption of dipoles at different temperatures onto a substrate of length  $L$ . The results reported here are mainly for  $L = 150a$ ; larger system sizes provided systematically equivalent results. We have selected the parameters  $\delta = a/2$ ,  $z_{in} = 15a$ , and  $z_{out} = 20a$ . These are conservative estimates; since dipolar interactions decay in average as  $r^{-3}$ , the energy diminishes more than 3 orders of magnitude from the neighborhood of the substrate to the launching height  $z_{in}$ . Higher values of  $z_{in}$  and  $z_{out}$  were tested, providing comparable results but dramatically increasing the computation time.

The presence of dipolar interactions is expected to induce changes in the structure of the adsorbed phase. We have investigated this point in  $(1+1d)$  by computing the density at jamming  $\theta_\infty$ , the pair correlation function  $g(r)$ , and a new quantity, the *chain-length density function*  $P(n)$ . The BM rule adopted for the final allocation of the dipoles allows an incoming particle to roll over another, adsorbing therefore close together and forming chains—sets of contiguous particles—in  $(1+1d)$  [15]. We define  $P(n)$  as the density of chains of length  $n$ , per unit length of substrate. This function is related to the jamming limit through  $\theta_\infty = \sum_{n=1}^{\infty} nP(n)$ .

In order to first check our algorithm, we have generated 1000 jammed configurations on a linear substrate of  $L = 750a$ , in the limit  $T_r \rightarrow \infty$  (free BM). We recover a jamming limit  $\theta_\infty^{BM} = 0.8079 \pm 0.0004$ , in excellent agreement with theoretical predictions  $\theta_\infty^{th} \approx 0.80865$  [8]. The REL and PAR models render in the most extreme case of  $T_r = 0$  (limit of zero temperature or infinitely strong interactions) the jamming limits  $\theta_\infty^{REL} = 0.855 \pm 0.002$  and  $\theta_\infty^{PAR} = 0.752 \pm 0.002$ , respectively. The difference with the BM value is rather notable, larger than a 5.7% and 7.0%, respectively. This feature should be contrasted with the small variations in the jamming limit due to the consideration of hydrodynamic interactions in the process (around 1.4%) [16].

Figure 1 depicts the pair correlation function  $g(r)$  for BM, and both models REL and PAR at  $T_r = 0$ . Model REL enhances greatly the maxima of  $g(r)$ , which occur at distances  $r_p = ap$ , for integer  $p$  (that is, corresponding to interparticle distances equal to a multiple of the diameter). We find in this case that the peaks decay exponentially, defining a correlation length of the form  $g^{REL}(r_p) \sim \exp(-r_p/\xi)$ . We estimate  $\xi = 4.73 \pm 0.04$ . In model PAR, on the other hand, correlations are strongly suppressed; the peaks in the function are almost invisible for  $r > 2a$ .

Given the expression (1) for the dipolar energy, it is energetically favorable for the particles to form linear chains

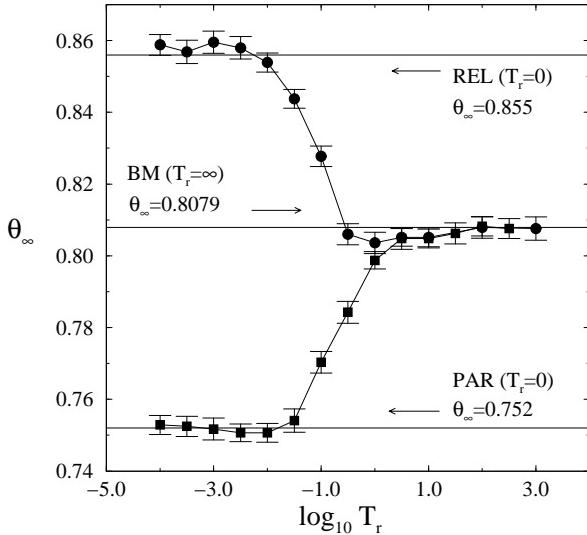


FIG. 3. Jamming limit  $\theta_\infty$  as a function of the reduced temperature  $T_r$  for the models REL (circles) and PAR (squares).

of aligned dipoles. This effect is studied in Fig. 2, where we have plotted  $P(n)$  for BM, and both REL and PAR at  $T_r = 0$ . We observe again an exponential decay for REL,  $P^{REL}(n) \sim \exp(-n/\bar{n})$ , with an estimated correlation size  $\bar{n} = 4.67 \pm 0.05$ , in good agreement with the characteristic length for the correlation function,  $\xi = 4.73$ . This exponential behaviour, on the other hand, is lost in BM and PAR; in those cases, the function  $P(n)$  decays much faster. The most characteristic property of Fig. 2 is the way in which the weight of the distribution moves towards larger chains in model REL (up to  $n = 24$ , which is almost 1/6 of the total substrate length). Large chains are, on the contrary, strongly suppressed in model PAR (only  $n = 5$ , 1/30 of the substrate length). The width of the chain-length distribution can be estimated by means of the average chain length  $\langle n \rangle$ ,

$$\langle n \rangle = \frac{\sum_{n=1}^{\infty} n P(n)}{\sum_{n=1}^{\infty} P(n)}. \quad (2)$$

We observe the values  $\langle n \rangle^{BM} = 1.857 \pm 0.003$ ,  $\langle n \rangle^{PAR} = 1.298 \pm 0.007$ , and  $\langle n \rangle^{REL} = 2.52 \pm 0.02$ .

The next point we have analyzed is the dependence of the relevant quantities of the models on the temperature. In Figure 3 we have plotted the jamming limit  $\theta_\infty$  for models REL and PAR, as a function of the reduced temperature  $T_r$ . A similar plot is made in Fig. 4 for the average chain length  $\langle n \rangle$ . From these two figures we conclude that, when increasing  $T_r$ ,  $\theta_\infty$  and  $\langle n \rangle$  jump rather discontinuously towards the limit value at high temperature (BM). This behaviour contrasts with the results reported for the diffusion-limited aggregation (DLA) of particles with dipolar interactions [13,14]. In those works, the fractal dimension of the aggregates was

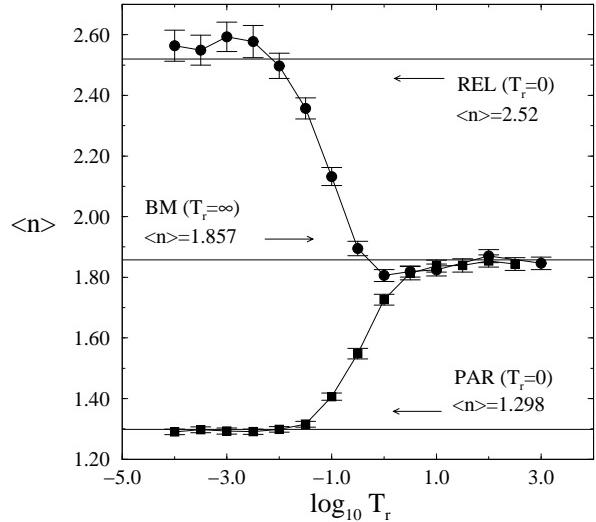


FIG. 4. Average chain length  $\langle n \rangle$  as a function of the reduced temperature  $T_r$  for the models REL (circles) and PAR (squares).

computed as a function of a reduced temperature  $T_r$ . It was found that the fractal dimension of dipolar DLA also changes between a high and a low temperature values, with a transition that seems to be continuous, taking place during almost 4 orders of magnitude in  $T_r$ . In the present case, however, we observe a transition occurring in a range of about 1.5 orders of magnitude in  $T_r$ . It seems therefore more likely the presence of a crossover in dipolar adsorption. The discontinuous nature of this crossover is smoothed by finite-size effects, but would be more evident in larger systems. We note that the crossover would happen at different characteristic temperatures  $T_c$  for the two models. In view of Figs. 3 and 4, we estimate the values  $T_c^{REL} \approx 10^{-1.25}$  and  $T_c^{PAR} \approx 10^{-0.5}$ .

Finally, in order to study the effects of dimensionality, we have considered the extension of our model to  $(1+2d)$ , by adsorbing dipolar particles onto a plane of size  $L \times L$ . In the case of free BM, we recover a jamming limit  $\theta_\infty = 0.609 \pm 0.003$ , in good agreement with previous simulations [9,10]. When introducing dipolar interactions at  $T_r < \infty$ , the algorithm turns out to be extremely time consuming, specially for model PAR. We report here preliminary results only for model REL at  $T_r = 0$ , on surfaces of a fairly small size ( $L = 10a$ ). Figure 5 depicts typical configurations in free BM and REL. The arrows drawn correspond to the projection onto the adsorption plane of the originally tridimensional dipoles. We can observe the local effect of the interactions, ordering the dipoles of neighboring particles in order to minimize the dipolar energy (1). The estimated value of the jamming limit is in the case REL  $\theta_\infty = 0.622 \pm 0.003$ . The difference with respect to the free case is 1.8%, smaller than that observed in  $(1+1d)$ . This is a result to be expected, since increasing the dimensionality increases the possibil-

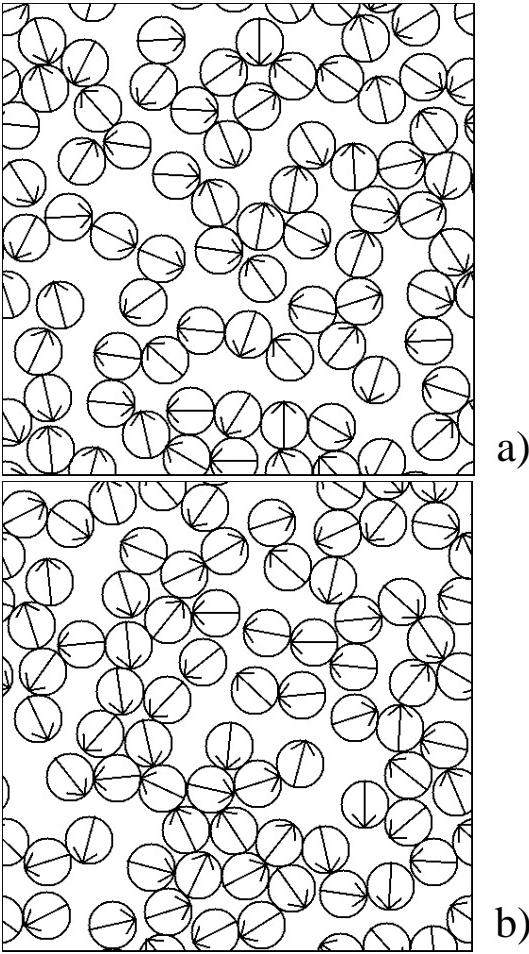


FIG. 5. Jammed configurations in a square of size  $L = 10a$ . a) Free BM. b) REL model. In this last case one can appreciate the relative tendency of neighbor dipoles to orient parallel to each other.

ties for disorder in the system. Therefore, the relative packing of the final state is expected to be smaller than in  $(1 + 1d)$ . A similar effect was also observed in 3d simulations of dipolar DLA [13].

In summary, we have shown that the presence of long range dipolar interactions during the adsorption process of particles on a substrate induces important changes in the structure of the adsorbed phase, reflected in the jamming limit, correlation function, and average chain length. In  $(1 + 1d)$ , one of the two models considered, namely relaxed dipoles (REL), shows long-range order, manifested in the tendency of the particles to form long chains, increasing therefore the packing of the substrate. On its turn, the model of parallel dipoles (PAR) produces smaller chains and results in a more disordered jammed phase. These results can be regarded as an effect of the different dynamics of the dipoles. Given the form of the dipolar energy (1), the adsorbed rigid dipoles in model PAR tend to repel an incoming particle approaching normally the surface; this fact induces an average repulsion

between particles and substrate. On the other hand, the relaxing dynamics in model REL results in an induced attraction between dipoles and surface, attraction responsible for the larger surface coverage. When decreasing temperature, we observe in model REL a transition from a disordered phase at high  $T_r$  to an ordered phase emerging at low temperatures; in model PAR the transition is reversed. In the  $(1 + 2d)$  geometry the effects are less pronounced, reflected in a slight variation of the jamming limit and an induced orientational order in the dipoles. Our findings may open further perspectives for the development of new models accounting for the phenomena we have reported and the different properties of the substrate, as well as a technical hint to achieve an increased efficiency of the adsorption processes, allowing the possibility of covering with particles a larger fraction of the surface.

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